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Electronic structure of the 1.429-eV complex neutral defect in GaAs from tunable-dye-laser spectroscopy

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Tunable-dye-laser excitation spectroscopy is applied to study the electronic properties of the 1.429-eV bound exciton (BE) in Cu-doped GaAs, presumably related to the Cu_{Ga}-As_{Ga} pair. A group of electronic states in the range 1.4285–1.432 eV are observed in more detail than in photoluminescence. BE states derived from both the $J=2$ and $J=1$ exchange-coupled multiplets are confined to this spectral region, but the detailed electronic structure is mainly determined by the low-symmetry local strain field. The nonaxial components of the local strain field are found to be important, while the exchange interaction is weaker than previously reported.

In a recent Rapid Communication preliminary data were reported on a photoluminescence (PL) and magneto-optical study of a complex neutral defect in Cu-doped GaAs with a bound exciton (BE) at 1.429 eV at 2 K.[1] This was apparently the first example of such a neutral ("isoelectronic") complex ever observed to bind an exciton in GaAs.[2] Very recently spin-triplet systems have been studied in GaAs, and it was concluded that they are related to excitons deeply bound to unidentified neutral complex defects.[3,4] The basic difficulty in localizing excitons at neutral defects in GaAs has been discussed elsewhere.[5] The 1.429-eV defect studied here is produced in Zn-doped bulk GaAs, and involves Cu (Refs. 1 and 6). The doping conditions necessary to produce this effect have been described elsewhere.[1,6] It is tentatively identified as a Cu_{Ga}-As_{Ga} substitutional pair.[1]

In this Rapid Communication we present a new series of experiments on the same defect, using tunable-dye-laser spectroscopy. Optical transmission was not sensitive enough to measure the absorption spectrum of this band exciton (BE), even in a sample with a 3-mm optical path. Using a tunable dye laser it has, however, been possible to observe this BE in absorption, via photoluminescence excitation (PLE) spectra. These measurements could also be done in a magnetic field, up to 7 T. These data give a more complete picture of the excited states of the BE than was possible from the PL data previously reported, leading to a somewhat revised picture of the electronic structure.

The experiments were performed with tunable-dye-laser excitation from a Styryl 9 dye, pumped by an Ar^+ laser. The samples were placed in a superconducting-magnet cryostat, where the temperature could be varied and a maximum magnetic field of 7 T could be obtained. The PL signal was detected through a Jobin-Yvon 1.5-m THR monochromator.

The low-temperature PL spectrum of the 1.429-eV BE was published in detail in Fig. 1 of Ref. 1, superimposed on a wing of a broad spectrum related to the Zn_{Ga} acceptor.[1] With tunable excitation the background from the Zn acceptor could be completely eliminated, but the details of the PL spectrum of the 1.429-eV BE remain as previously published.[1] Only one electronic PL line is observed at 2 K, but at elevated temperatures two additional broadened lines appear (Fig. 1 of Ref. 1). In the PLE spectra the entire electronic BE spectrum is revealed, even at the lowest temperature, as seen in Fig. 1(a). This is of great advantage, since the whole spectrum can then be studied at the lowest temperature, where the linewidth is much smaller than, e.g., at 10 K.[1] The linewidth in Fig. 1(a) is about 0.16 meV for the lowest-energy lines.

From a comparison of PLE spectra measured at different temperatures in a magnetic field, it is found that the intensity ratio between the observed electronic transitions remains constant; only thermal broadening occurs at elevated temperatures. This is in sharp contrast to the case of PL, where strong thermalization occurs between the BE states.[1] The absence of such thermalization in PLE definitely proves the assumption that the ground state of the BE transition is a $J=0$ state. This is most naturally interpreted in terms of a neutral (isoelectronic) defect, with no electronic particle bound in the ground state, as also assumed in Ref. 1. It should be noted, however, that thermalization in PL would occur even if the de-

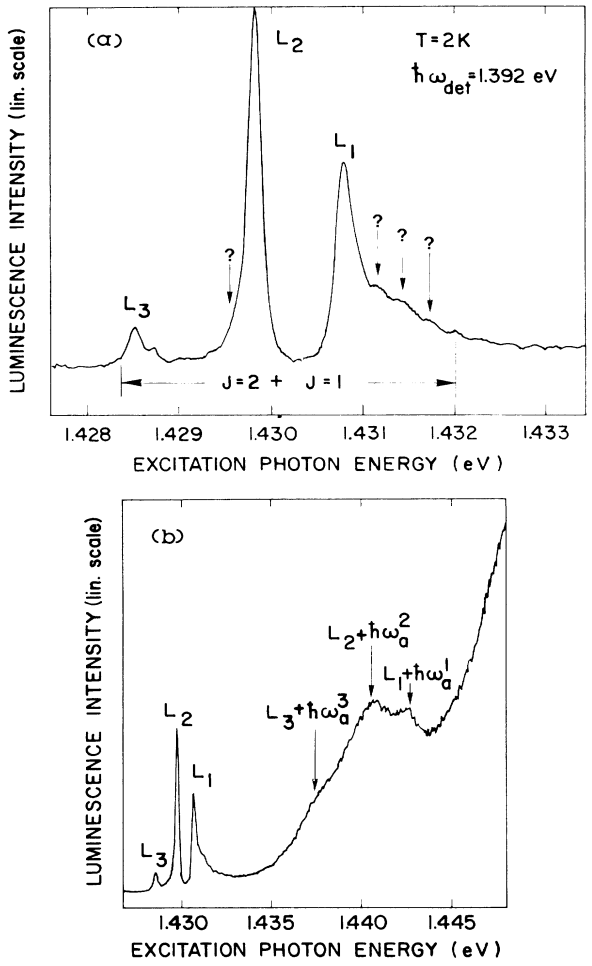

FIG. 1. (a) Low-temperature photoluminescence excitation (PLE) spectrum of the 1.429-eV bound exciton (BE) in GaP:Zn,Cu, obtained with a Styryl 9 dye. The positions of the eight expected BE lines in a low symmetry are indicated in the figure, some are not well resolved, and these are indicated by question marks. (b) The same spectrum as in (a), but for an extended photon energy range. The three main lines of the BE are well resolved, and the three lines around 1.44 eV are interpreted as phonon replica, involving a quasilocalized phonon mode $\hbar\omega_a$, also seen in the photoluminescence spectrum (Ref. 1). The energies of the phonons $\hbar\omega_a^1$, $\hbar\omega_a^2$, and $\hbar\omega_a^3$ associated with L_1–L_3, respectively, differ slightly.

fect was a donor or an acceptor, so that the PLE experiment is necessary to prove the electrical nature of the defect.

The spectrum in Fig. 1(a) also reveals the relative oscillator strengths of the different electronic components of the 1.429-eV BE, which could not be obtained from PL data.[1] The two lowest components (called $L3$ in Ref. 1) at 1.4285 and 1.4287 eV, respectively, are separately resolved already at zero field in the PLE data, in contrast to PL data.[1] The $L2$ component at ≈ 1.4299 eV is very strong, about a factor 10 stronger than $L3$. The most interesting feature of Fig. 1(a) is the region of the $L1$ line at about 1.431 eV. This line is broader than the other lower-energy lines, and it has a wing toward higher energy with two or three additional unresolved peaks [Fig. 1(a)]. The obvious conclusion is that already at zero field a considerably larger number of lines is present in the spectral region 1.4285–1.432 eV [eight lines are indicated in Fig. 1(a)], compared to the five lines from PL data, discussed in Ref. 1.

The PLE spectrum measured over a somewhat broader photon energy range is shown in Fig. 1(b). This spectrum proves that no electronic lines belonging to the lowest multiplet of BE states ($J=1$ plus $J=2$ states) occur above 1.432 eV. In the one-phonon range rather strong phonon coupling is observed, as is also seen in PL emission. The three discrete phonon modes observed around 1.44 eV in Fig. 1(b) correspond to the 9-meV mode at 1.419 eV in the PL emission spectrum at 2 K,[1] although the phonon energies in absorption (PLE) are slightly different, and also vary for the corresponding electronic lines [Fig. 1(b)]. PLE spectra were measured for photon energies up to the band gap, but no additional sharp electronic features associated with the 1.429-eV BE could be observed. This is consistent with the general model for the electronic structure of the BE presented in Ref. 1, predicting that the eight electronic BE states derived from a $J=\frac{3}{2}$ hole and and a spinlike electron are all contained within 3–4 meV from the lowest BE state.[1] One might expect, according to the Hopfield-Thomas-Lynch (HTL) model,[7] for an electron-attractive defect, to observe excited states derived from single-particle excitations of the more shallow particle, i.e., the bound hole in this case,[1] similar to what has been observed for nearest-neighbor pairs in GaP.[8] No such excited states are observed below the band-gap energy. The bound hole may be more localized in this case, unlike a shallow acceptor hole, in which case, this BE is not a typical HTL case.

The Zeeman data in PLE have been taken for fields up to 7 T in the Voigt configuration, but the spectral resolution at 7 T is insufficient to resolve all the details of the spectrum because of a larger number of partly overlapping lines. Nevertheless a full angular dependence study has been performed at 7 T and 2 K. The data for the energy region $h\nu < 1.430$ eV agree approximately with what was observed in PL.[1] Actually, this part of the spectrum is much more conveniently studied in PL, due to the thermalization that favors the intensity of the lower-energy lines in PL. The two upper sets of lines called $L2$ and $L1$, respectively, in Ref. 1, can in principle be studied much more accurately in PLE, although the spectral resolution at 7 T is still incomplete. The strong middle line ($L2$) in the spectrum at ≈ 1.4299 eV, is quite isotropic in its angular dependence. The region around the $L1$ line, on the other hand, shows some appreciable structure in the magnetic field, but the detailed behavior of this region, including the upper weaker lines between 1.431–1.432 eV in Fig. 1, could not be fully resolved at 7 T.

The PLE and Zeeman data in this work confirm the earlier analysis of this BE as associated with a strongly electron-attractive local potential, for a defect with ⟨110⟩ symmetry. In Ref. 1 it was supposed that the three main lines observed at zero field in PL were all derived from the $J=2$ quintuplet of an exchange-coupled electron-hole

pair, while the $J=1$ part of the spectrum was not observed, being slightly shifted toward higher energies by the electron-hole (e-h) exchange interaction.[1] This picture needs revision in the light of our novel data, and it seems clear that the $J=1$ and $J=2$ components are strongly mixed by the local strain field. If the weak components in Fig. 1(a) are accounted for in the analysis, the low defect symmetry manifests itself via a rather strong nonaxial local-strain-field term in the zero-field Hamiltonian, in addition to the axial term included in the analysis of Ref. 1. The zero-field Hamiltonian employed in Ref. 1 should be replaced by

$$H_{\rm ex}+H_{\rm LCF}=-a\mathbf{J}_h\cdot\mathbf{s}_e-b(J_{hx}^3 s_{ex}+J_{hy}^3 s_{ey}+J_{hz}^3 s_{ez}) -D[J_{h\zeta}^2-\tfrac{1}{3}J_h(J_h+1)]-E(J_{h\xi}^2-J_{h\eta}^2)\ , \quad (1)$$

where the E parameter is a measure of the strength of the nonaxial part of the local strain field [local crystal field (LCF)]. This Hamiltonian can give rise to a splitting into eight electronic lines at zero magnetic field, all at least partly resolved in Fig. 1(a). The revised analysis of data results in a similar magnitude for the D and E parameters, both of the order 1 meV. The exchange parameters were overestimated in Ref. 1. From the knowledge of the energies of all lines, it is clear that the a parameter is about 1 meV, i.e., approximately half the value reported in Ref. 1, while the b value is found to be close to zero. However, in this revised analysis, the g values of the electron and the hole remain essentially as reported in Ref. 1. Considerably higher magnetic fields will be needed to completely resolve the entire Zeeman spectrum of this BE, which is necessary to achieve an accurate determination of all parameters in the Hamiltonian.

It should be noted also that oscillator strengths of these lines cannot be predicted very reliably, treating the local strain field as a perturbation,[9] since the mixing between the different exchange-coupled electronic BE components in a strong low-symmetry strain field is quite strong.

It is interesting to compare the electronic structure of the Cu_{Ga}-As_{Ga} defect BE in GaAs with the corresponding BE spectrum for the deep midgap ⟨110⟩-oriented Cu_{Ga}-P_{Ga} defect in GaP, which has recently been studied by PL and optically detected magnetic resonance.[10] Although the Cu_{Ga}-P_{Ga} defect in GaP is also a dominantly electron-attractive defect, the lowest BE state in that case is a spin triplet ($S=1$). This is presumably the result of the combined effect of a larger spin-orbit interaction in GaAs for the bound-hole states, and a more delocalized wave function for bound holes at Cu_{Ga}, as compared to GaP.[11]

In summary, we have reported on the application of tunable-dye-laser excitation spectroscopy to the study of the electronic structure of the 1.429-eV bound exciton in GaAs. The data confirm the previous assumption that the defect is a neutral isoelectronic complex (assumed to be the Cu_{Ga}-As_{Ga} substitutional pair). No single-particle excitations of the secondary bound particle (hole) can be observed. These data establish the strong effects of the local strain field on the detailed electronic structure of the BE lines in the region 1.4285–1.432 eV; the nonaxial strain components also need to be accounted for, in order to explain the experimental absorption (PLE) data in the no-phonon region. The level splitting due to electron-hole exchange interaction is smaller than previously predicted, and is comparable to the strain splitting of the BE levels.

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